

## Free Radical Polymerization of Methyl Methacrylate under Multi-site Phase-transfer Catalyst - A Kinetic Study

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### ABSTRACT

The kinetics and mechanism of free radical polymerisation of methyl methacrylate (MMA) using water soluble initiator viz., potassium peroxydisulphate (PDS) in the presence of newly synthesized 1,4-dihexadecylpyrazine-1,4-dium dibromide (MPTC) as multi-site phase-transfer catalyst (MPTC) has been investigated in ethyl acetate / water two phase system at constant temperature  $50 \pm 1^\circ\text{C}$  under nitrogen atmosphere. The effect of variation of [MMA], [PDS], [MPTC], and volume of fraction of aqueous phase, solvent polarity and temperature on the rate of polymerisation ( $R_p$ ) was ascertained. The order with respect to monomer, initiator and multi-site phase-transfer catalyst were found to be 1.0, 0.5 and 0.5 respectively. The rate of polymerisation of is independent of ionic strength and pH. Based on results obtained, a suitable kinetic scheme has been proposed to account for the experimental observations and its significance was discussed.

**Keywords:** Kinetics, multi-site phase-transfer catalyst, radical polymerization, methyl methacrylate, perdisulphate, initiator.

### INTRODUCTION

Phase-transfer catalysis technique was first introduced in the 1960s as a convenient and highly useful tool to carryout the reactions between the two mutually

immiscible reactants that generally do not have a common solvent. Phase-transfer catalyst (PTC) has a capability to carry one of the reactants from its normal phase (generally aqueous phase) into the other phase (organic phase) where the reaction

takes place and to give a high conversion and selectivity for the desired product under mild reaction conditions<sup>1</sup>. The advantages of PTC system are simplicity, mild reaction conditions, use of inexpensive, recoverable and non toxic solvents, a lower reaction temperature and use of water with an organic solvent as reaction medium. The extensive range of reactions such as anion displacement reactions, oxidation reduction, elimination, alkylation, acrylation and hydrolysis could be enhanced powerfully with the help of phase-transfer catalysts. In the application of polymerization reactions they have been employed in condensation polymerization<sup>2</sup>, anionic polymerization<sup>3, 4</sup>, copolymerization<sup>5,6</sup>. Also, PTC plays an important role in manufacturing processes of specialty chemicals such as pharmaceuticals dyes, perfumes, and additives for lubricants, pesticides and monomer preparation for polymer synthesis<sup>7-9</sup>.

Many authors reported the use of single site phase transfer catalyst for free radical polymerization of vinyl monomers in aqueous organic biphasic medium such as butyl acrylate (BA)<sup>10-12</sup> methyl methacrylate (MMA)<sup>13-17</sup>, Acrylonitrile (AN)<sup>18,19</sup> methyl acrylate (MA)<sup>20</sup>, Glycidyl methacrylate (GMA)<sup>21</sup>, Butyl methacrylate (BMA)<sup>22</sup>, Ethyl methacrylate (EMA)<sup>23</sup> etc.

The first report published on multi – site phase transfer catalyst was by Idux et al., and they have synthesized phosphonium and quaternary ammonium ions containing more than one site per molecule<sup>24</sup>. Many others studied and reported different multisite PTCs for various organic reactions<sup>25-32</sup>.

The survey of literature on this technique reveals that, so far, very few

reports are available in free radical polymerization of vinyl esters under multi-site phase transfer catalysis condition. Murugesan vajjiravel *et al.*<sup>33,34</sup> reported the heterogeneous catalysis by new polymer-supported multisite phase transfer catalysts. Balakrishnan and Muniraj<sup>35</sup> reported kinetics of polymerisation ortho-, meta-, and para-tolymethacrylates and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>/TBBA (tetra butyl ammonium bromide) – assisted free – radical polymerisation. In this paper, we report the results of kinetics of free radical polymerization of methyl methacrylate (MMA) using potassium peroxydisulphate (PDS) as water soluble initiator and synthesized 1,4-dihexadecyl pyrazine-1,4-diium dibromide (MPTC) as multi-site phase- transfer catalyst in ethyl acetate/ water two phase system.

## EXPERIMENTAL

### Materials

Methyl methacrylate (SD's, Bombay, India) was washed with 5% NaOH solution to remove the inhibitor and with double distilled water to remove the basic impurities and then dried over calcium chloride and distilled under reduced pressure. The initiator PDS (Merch, Mumbai, India), ethyl acetate (CDH, New Delhi, India) and methanol (SRL, Mumbai, India) were used as received. The multi-site phase-transfer catalyst viz., 1,4-dihexadecylpyrazine-1,4-diium dibromide (MPTC) was synthesized by the following procedure.

### Synthesis of multi-site phase-transfer catalyst (MPTC)

In a 250 mL three-necked round bottom flask, a measured quantity of one equivalent of pyrazine and two equivalent of hexadecyl bromide (1:2.2 molar ratios) was taken. To this mixture 40 mL of ethanol was added slowly and then the solution was stirred and refluxed under nitrogen atmosphere for 10 hours. After the reaction time, the excess solvent was removed by vacuum evaporator and thus formed disite PTC viz., 1,4-dihexadecylpyrazine-1,4-diium dibromide (MPTC). This in turn was repeated washed with ether (4x25 mL) and dried and stored in a desiccator (Scheme 1). The yield was 0.78 mol. FT – IR (KBr,  $\text{cm}^{-1}$ ): 1178 ( $\text{C-N}^+$  stretching), 3106 (aromatic C-H stretching), 2932 (aliphatic C-H stretching), 1392 and 1473 (C-H bending);  $^1\text{H}$  NMR (400  $\text{MHz}$ ,  $\text{CDCl}_3$ ):  $\delta$  0.77 (3H), 1.16 (16H), 1.19 (2H), 1.77 (4H), 3.30 (2H);  $^{13}\text{C}$  NMR (100  $\text{MHz}$ ,  $\text{CDCl}_3$ ):  $\delta$  13.96, 18.26, 22.45, 22.50, 26.12, 28.05, 28.60, 28.80, 28.90, 30.10, 31.52, 31.62, 32.73, 34.03, 50.11, 53.05, 128.68; Elemental analysis Calc. C, 62.60; H, 10.21; N, 4.06. Found: C, 62.51; H, 10.11, N, 4.01.

### Polymerization Procedure

The polymerisation reactions were carried out in an inert atmosphere at  $50 \pm 1^\circ\text{C}$ . The reaction mixture consists of 10 mL of aqueous phase and 10 mL of organic phase. The monomer in ethyl acetate solvent was the organic phase. The catalyst, potassium sulphate (for adjusting ionic strength) and sulphuric acid (for maintaining  $\text{H}^+$ ) were taken in the aqueous phase. The reaction mixture was thoroughly deaerated

for 30 min. when potassium peroxydisulphate (PDS) was added to the reaction mixture, polymerization started and polymethyl methacrylate precipitated continuously during polymerization without stirring or agitation. The polymerisation reactions were arrested by pouring reaction mixture into ice-cold methanol containing traces of hydroquinone. The precipitate was filtered through a G3 sintered crucible, washed with distilled water and methanol, dried in a vacuum oven at  $50^\circ\text{C}$ . The rate of polymerisation ( $R_p$ ) was calculated from the weight of the polymer formed.

$R_p$  was calculated from the weight of polymer obtained using the following formula:

$$R_p = \frac{1000 W}{V.t.M.}$$

Where

W - Weight of the polymer in grams

V - Volume of the reaction mixture in mL

t - Reaction time in seconds

M - Molecular weight of the monomer

In the figures, apparent deviation from linear relationship may attribute to gravimetric data handling analysis. However the conversion was restricted to less than twenty percentage in all kinetic studies because above twenty percentage kinetics would not obeyed.

### Instruments

The Viscosity average molecular weight ( $M_v$ ) of the polymer was determined in benzene at  $30 \pm 1^\circ\text{C}$  with an Ubbelohde viscometer using Hark-Houwink equation<sup>23</sup>.

$$\eta = K (Mv)^{\alpha}$$

Where

K -  $20.9 \times 10^{-3}$

$\alpha$  - 0.75

$\eta$  - Refers to intrinsic viscosity

Mv - Refers to the viscosity average molecular weight of the polymer.

From the molecular weight of the polymer, the degrees of polymerisation (Pn) values were calculated.

## RESULTS AND DISCUSSION

The free radical polymerization of MMA initiated by PDS – Multi – Site phase-transfer catalyst in ethyl acetate / water biphasic was studied under different experimental conditions to evaluate the various parameters which affects the polymerization reaction.

### Steady state Rate of polymerization

The steady state rate of polymerization for the MMA was studied by determining Rp at different intervals of time. The plot of Rp vs Time shows that the steady state rate of polymerization of the MMA was obtained at 50 min. So the polymerization reaction time was fixed for 50 min to carry out the experiments with variation of other parameters. (Table 1, Fig.1)

### Effect of monomer concentration On Rp

The effect of concentration on the rate of polymerization (Rp) was studied at various concentrations of monomers from 1.0 to 4.0 mol dm<sup>-3</sup> keeping the concentration of PDS, MPTC, ionic strength

and pH constant. Rp increases with increase in the concentration of the monomer. The reaction order with respect to monomer concentration was determined from the plot of (5 + log Rp) vs (1+ log [MMA]) and it was found to be 0.98~1.0 (Fig 2). The plot of Rp vs [MMA]<sup>1.0</sup> passing through the origin confirms the above observations (Table 2, Fig.3). A similar order of unity with respect to monomer has been reported by Murugesan *et al.*<sup>36</sup> and Maruthamuthu *et al.*<sup>37</sup> and many other authors<sup>38, 39</sup> in the phase-transfer assisted polymerisation of MMA under heterogenous condition using PDS as the initiator. A high reaction of order 1.5 with respect to [monomer] was also reported by Ghosh and Mandal<sup>40</sup> in the solution polymerization of MMA using ion-paired trioctylmethylammonium- persulphate initiator in ethyl acetate solvent.

### Effect of PDS concentration on Rp

At fixed reaction condition, the rate of polymerization increased with an increase in concentration of PDS (K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) (0.01-0.08 moldm<sup>-3</sup>) Rp was found to increase with increasing concentration of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>. From the plot of (5+log Rp) Vs (1+log [K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>]) the slope is found to be 0.49~0.5 (Fig.4). The order was confirmed by plotting Rp Vs [K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>]<sup>0.5</sup> is passing through the origin with respect to initiator concentration (Table-3, Fig.5). A reaction order of 0.5 with respect to [PDS] was reported by Yoganand *et al.*<sup>41</sup> in the polymerization of MMA initiated by PDS, 14-bis (dimethylpentyl) ethylene diammonium bromide as disite phase-transfer catalyst system.

### Effect of PTC concentration on $R_p$

The effect of concentration of multi-site phase-transfer catalyst, MPTC on the rate of polymerization was studied by varying its concentration in the range of 0.01 to 0.08 mol.dm<sup>-3</sup> at fixed concentration of other parameters.  $R_p$  increases with increase in concentration of MPTC. The plot of (5+ log  $R_p$ ) vs (1+ log [MPTC]) was found to be 0.49~0.5 (Fig.6). It was confirmed by plotting  $R_p$  Vs [MPTC]<sup>0.5</sup> passing through origin with respect to [MPTC] (Table-4, Fig.7). However the polymerization rate tends to level off at high MPTC concentrations. In the absence of PTC, the polymerization reaction is not observed even after several hours. The half order dependence of  $R_p$  with respect to PTC has been reported by Umapathy *et al.* in the phase-transfer catalyst assisted polymerization of vinyl monomers<sup>42,43</sup>. However Mandal *et al.*<sup>44</sup>, reported a first order dependence of  $R_p$  on [Bu<sub>4</sub>NBr] in the polymerization of MMA. Bulacovschi *et al.*<sup>45</sup> studied the kinetics of polymerization of MMA using the K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> – Arquad catalyst system in benzene –water media. From the literature survey it reveals that there is no standard order for phase –transfer catalyst with same monomer. It depends upon the reaction condition as well as other reactant parameters.

### Effect of Ionic strength ( $\mu$ ) on $R_p$

The effect of ionic strength on  $R_p$  has been investigated by varying ionic strength using K<sub>2</sub>SO<sub>4</sub> in the range 0.001-0.002, keeping other variables such as [monomer], [PDS], [PTC] and pH constant. The variation of ionic strength had no

significant changes in the rate of polymerisation.

### Effect of [H<sup>+</sup>] variation on $R_p$

The effect of [H<sup>+</sup>] variation was observed by varying the H<sup>+</sup> ion concentration in the range of 0.001 - 0.002 mol.dm<sup>-3</sup>. The variation of [H<sup>+</sup>] is found to exert no appreciable effect on  $R_p$  for MMA.

### Effect of temperature on $R_p$

The effect of variation of temperature from 50°C to 65°C on the rate of polymerization was studied by keeping other parameters constant. The rate of polymerization increases with increase in temperature. From the slope of Arrhenius plot of log  $R_p$  vs 1/T, the over all activation energy of polymerization ( $E_a$ ) for the MMA system is calculated (Table 5, Fig.8). From the value of activation energy the other thermodynamic parameters such as entropy of activation ( $\Delta S^\ddagger$ ), enthalpy of activation ( $\Delta H^\ddagger$ ) and free energy of activation ( $\Delta G^\ddagger$ ) have been calculated using Eyring plot (log  $R_p/T$  vs 1/T) and given below.

$E_a$ , kJ / mol	$\Delta G^\ddagger$ , kJ /mol	$\Delta H^\ddagger$ , kJ /mol	$\Delta S^\ddagger$ , eu
27.26	74.80	24.57	- 155.52

### Effect of volume fraction of aqueous phase on $R_p$

Polymerization reaction were conducted with a constant volume of organic

phase and different volumes of aqueous phase ( $V_w/V_o = 0.61 - 1.00$ ) at fixed concentrations of all other parameters. A small increase in rate of polymerization was observed with increase in the volume of the aqueous phase. From the plot of  $(5+\log R_p)$  vs  $1+\log (V_w/V_o)$  in (Fig 9), the reaction order with respect to  $(V_w/V_o)$  was found to be 0.050 (Table-6). Mandal *et al.*<sup>26</sup> reported the value of 0.15 for the order with respect to  $V_w/V_o$  in the polymerisation of MMA initiated by  $K_2S_2O_8$ - $Bu_4NBr$  catalyst system. Balakrishnan *et al.*<sup>30</sup> observed the reaction exponents with respect to  $V_w/V_o$  in the polymerisation of MMA in the range of 0.3-0.4 with  $K_2S_2O_8$  initiator and different phase-transfer catalysts such as tetramethylammonium bromide ( $Me_4NBr$ ), tetraethylammonium bromide ( $Et_4NBr$ ) and benzyltriethylammonium chloride (BTEAC).

#### Effect of solvents polarity on $R_p$

The effect of solvent on  $R_p$  was examined by carrying out the polymerization reaction for MMA in six different solvents viz., benzene, toluene, chlorobenzene, cyclohexane, ethyl acetate and cyclohexanone. It was found that the  $R_p$  decreased in the following order:

Cyclohexanone > ethyl acetate >  
cyclohexane > toluene > benzene >  
chlorobenzene

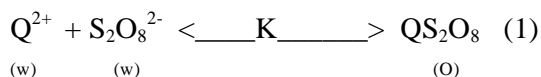
The increase in the rate of polymerization may be due to the increase in the polarity of the medium, which facilitates greater transfer of peroxy disulphate to the organic phase (Table-7).

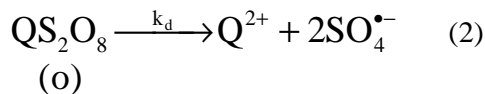
#### MECHANISM AND RATE LAW

In the present investigation, Potassium perdisulphate (PDS) as the water soluble initiator, is migrated from the aqueous phase to the monomer containing organic phase is facilitated by the name (MPTC) which serves as the phase transfer agent. Rasmussen and Smith<sup>31,32</sup> studied that the presence of 18-crown-6 and quaternary ammonium salts as the phase-transfer agent accelerate the rate of transfer of PDS from the aqueous phase to monomer phase. They also observed that the formation of quaternary peroxydisulphate complex ( $Q_2S_2O_8$ ), which was soluble in organic medium, was responsible for the rapid polymerization of monomers like butyl acrylate<sup>32,33</sup>. Thus, the quaternary ammonium salts transfer the PDS ion from aqueous phase to organic phase and enhances the rate of decomposition of  $S_2O_8^{2-}$  to sulfate ion radicals which initiates the polymerization. Based on the kinetic results the following mechanism has been proposed for the polymerization of MMA.

The following reactions characterizing the polymerization of methyl methacrylate (M) initiated by  $K_2S_2O_8$ /MPTC in ethyl acetate/ water two- phase systems. It is assumed that dissociation of quaternary salt QX and  $K_2S_2O_8$ , formation of  $QS_2O_8$  in aqueous phase, and initiation of monomer in organic phase occurs by the following reactions.

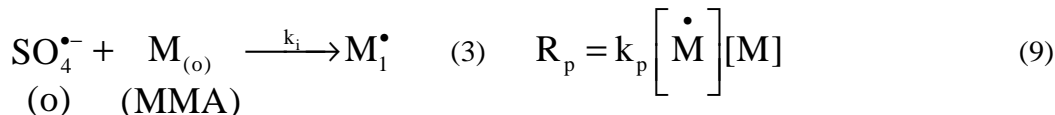
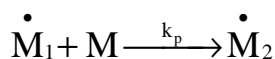
##### (a) Phase Transfer



**(b) Initiation**

$$R_i = \frac{d[SO_4^{\bullet-}]}{dt} = 2k_d K [Q^{2+}]_w [S_2O_8^{2-}]_w \quad (8)$$

The rate of propagation is given by

**(c) Propagation**

$$\left[ \dot{M} \right] = \frac{R_p}{k_p [M]} \quad (10)$$

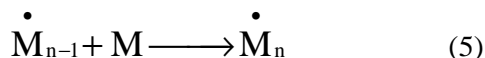
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(4) The rate of termination ( $R_t$ ) is given by

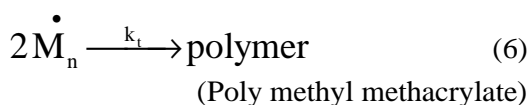
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$$R_t = 2k_t \left[ \dot{M} \right]^2 \quad (11)$$



(d) The termination occurs by the combination of two growing polymer chain radicals, it can be represented as



At steady state, the rate of initiation equals to rate of termination i.e.,

$$R_i = R_t \quad (12)$$

$$2k_d K [Q^{2+}]_w [S_2O_8^{2-}]_w = 2k_t [M^{\bullet}]^2 \quad (13)$$

$$\left[ \dot{M} \right]^2 = \frac{k_d K [Q^{2+}]_w [S_2O_8^{2-}]_w}{k_t} \quad (14)$$

The subscripts (o) and (w) refer to organic phase and aqueous phase respectively.

$$\left[ \dot{M} \right] = \left[ \frac{k_d K [Q^{2+}]_w [S_2O_8^{2-}]_w}{k_t} \right]^{\frac{1}{2}} \quad (15)$$

Applying the general aspects of free radical polymerization and stationary state hypothesis to the radical species, the rate law for this mechanism can be derived as follows:

The rate of initiation is given by

$$R_i = k_i [M] [SO_4^{\bullet-}] \quad (7)$$

Using Eqs. 10 and 15, the rate of polymerization represented as follows.

$$R_p = k_p \left[ \frac{k_d K}{k_t} \right]^{\frac{1}{2}} [Q^{2+}]_w^{0.5} [S_2O_8^{2-}]_w^{0.5} [M]^1 \quad (16)$$

The above equation satisfactorily explains all the experimental observations.

#### Dependence of $\bar{P}_n$ on $K_2S_2O_8$

The expression for the degree of polymerization is

$$\bar{P}_n = \frac{R_p}{R_t} \quad (17)$$

$$\bar{P}_n = \left[ \frac{k_p[M]}{2(Kk_t k_d)^{\frac{1}{2}} [Q^{2+}]_w^{0.5} [S_2O_8]_w^{0.5}} \right] \quad (18)$$

$$\frac{1}{\bar{P}_n} = \left[ \frac{2(Kk_t k_d)^{\frac{1}{2}} [Q^{2+}]_w^{0.5} [S_2O_8]_w^{0.5}}{k_p[M]} \right] \quad (19)$$

Accordingly, the degree of polymerization  $\bar{P}_n$  directly proportional to  $[M]$  and inversely proportional to the square root of  $[K_2S_2O_8]$  and  $[MPTC]$ . It is found that a plot of  $1/\bar{P}_n$  Vs  $[M]^1$ ,  $1/\bar{P}_n$  Vs  $[S_2O_8]^{0.5}$  and  $1/\bar{P}_n$  Vs  $[MPTC]^{0.5}$  gives a straight line passing through the origin for MMA system. (Tables 8,9,10 and figure 9, 10, 11).

**Table 1**  
**Steady State Rate of Polymerization**

Time (min)	$R_p \times 10^4, \text{mol dm}^{-3} \text{s}^{-1}$
5	0.5951
15	0.9859
25	1.2563
35	1.4124
45	1.3648
55	1.2852
65	1.2781
75	1.2550

Reaction condition:  $[MMA]$ ,  $2.5 \text{ mol dm}^{-3}$ ;  $[K_2S_2O_8]$ ,  $2.0 \times 10^{-2} \text{ mol dm}^{-3}$ ;  $[MPTC]$ ,  $2.0 \times 10^{-2} \text{ mol dm}^{-3}$ ;  $[H^+]$ ,  $0.2 \text{ mol dm}^{-3}$ ;  $[\mu]$ ,  $0.05 \text{ mol dm}^{-3}$ ; Temp.  $50^\circ\text{C}$



**Table 2**  
**Effect of monomer concentration on Rp**

[MMA], mol dm <sup>-3</sup>	Rp x 10 <sup>4</sup> , mol dm <sup>-3</sup> s <sup>-1</sup>	1+ log [MMA]	5 + log [Rp]
1	0.5286	1.0000	0.7231
1.5	0.7224	1.1761	0.8588
2	0.9687	1.3010	0.9862
2.5	1.2826	1.3979	1.1081
3	1.3456	1.4771	1.1289
3.5	1.7191	1.5441	1.2353
4	2.1018	1.6021	1.3226

Reaction condition : [K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>] ,2.0 x10<sup>-2</sup> mol dm<sup>-3</sup>; [ MPTC ], 2.0 x10<sup>-2</sup> mol dm<sup>-3</sup>;  
[ H<sup>+</sup> ], 0.2 mol dm<sup>-3</sup>; [μ ], 0.05 mol dm<sup>-3</sup>; Temp, 50° C; Time , 50 min

**Table 3**  
**Effect of PDS concentration on Rp**

[K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> ] x 10 <sup>2</sup> , mol dm <sup>-3</sup>	[K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> ] <sup>0.5</sup> x10 <sup>2</sup> , mol dm <sup>-3</sup>	Rp x 10 <sup>4</sup> , mol dm <sup>-3</sup> s <sup>-1</sup>	1+ log [K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> ]	5 + log [ Rp ]
1	10	0.9318	1.0000	0.9693
2	14.14	1.2286	1.3010	1.0894
4	20	1.7604	1.6021	1.2456
5	22.36	1.9351	1.6990	1.2867
6	24.49	2.2243	1.7782	1.3472
8	28.28	2.5793	1.9031	1.4115

Reaction condition : [MMA] , 2.5 mol dm<sup>-3</sup>; [ MPTC ], 2.0 x10<sup>-2</sup> mol dm<sup>-3</sup> [ H<sup>+</sup> ], 0.2 mol dm<sup>-3</sup>; [μ ], 0.05 mol dm<sup>-3</sup>; Temp, 50° C; Time, 50 min

**Table 4**  
**Effect of [MPTC] concentration on Rp**

[MPTC] $\times 10^2$ , mol dm <sup>-3</sup>	[MPTC] <sup>0.5</sup> $\times 10^2$ , mol dm <sup>-3</sup>	Rp $\times 10^4$ , mol dm <sup>-3</sup> s <sup>-1</sup>	1+ log [MPTC]	5+ log [Rp]
1	10	1.1990	1.0000	1.0788
2	14.14	1.6372	1.3010	1.2141
4	20	2.3030	1.6021	1.3623
5	22.36	2.5067	1.6990	1.3991
6	24.49	2.9936	1.7782	1.4762
8	28.28	3.3643	1.9031	1.5269

Reaction condition : [MMA], 2.5 mol dm<sup>-3</sup>; [K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>], 2.0  $\times 10^{-2}$  mol dm<sup>-3</sup>; [H<sup>+</sup>], 0.2 mol dm<sup>-3</sup>; [ $\mu$ ], 0.05 mol dm<sup>-3</sup>; Temp, 50°C; Time, 50 min.

**Table 5**  
**Effect of Temperature on Rp**

Temperature, K	Rp $\times 10^4$ , mol dm <sup>-3</sup> s <sup>-1</sup>	1/T $\times 10^3$ , K <sup>-1</sup>	5 + log [Rp]
313	1.5675	3.1949	1.1952
318	1.8387	3.1447	1.2645
323	2.2537	3.0960	1.3529
328	2.5067	3.0488	1.3991
333	2.9465	3.0030	1.4693
338	3.3986	2.9586	1.5313

Reaction condition : [MMA], 2.5 mol dm<sup>-3</sup>; [K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>], 2.0  $\times 10^{-2}$  mol dm<sup>-3</sup>; [MPTC], 2.0  $\times 10^{-2}$  mol dm<sup>-3</sup>; [H<sup>+</sup>], 0.2 mol dm<sup>-3</sup>; [ $\mu$ ], 0.05 mol dm<sup>-3</sup>; Time 50 min

**Table 6**  
**Effect of aqueous phase volume on Rp**

$V_w / V_o$	$1 + \log ( V_w / V_o )$	$R_p \times 10^4,$ $\text{mol dm}^{-3}\text{s}^{-1}$	$5 + \log [ R_p ]$
0.61	0.7853	1.4158	1.1510
0.67	0.8261	1.4227	1.1531
0.75	0.8751	1.4296	1.1552
0.82	0.9138	1.4358	1.1571
0.92	0.9638	1.4438	1.1595
1	1.000	1.4518	1.1619

Reaction condition : [MMA],  $2.5 \text{ mol dm}^{-3}$ ;  $[\text{K}_2\text{S}_2\text{O}_8]$ ,  $2.0 \times 10^{-2} \text{ mol dm}^{-3}$ ; [MPTC ],  $2.0 \times 10^{-2} \text{ mol dm}^{-3}$ ;  $[\text{H}^+]$ ,  $0.2 \text{ mol dm}^{-3}$ ;  $[\mu]$ ,  $0.05 \text{ mol dm}^{-3}$ ; Temp,  $50^\circ\text{C}$ ; Time 50 min.

**Table 7**  
**Effect of solvent polarity on Rp**

Reaction conditions	$R_p \times 10^4, \text{mol dm}^{-3} \text{s}^{-1}$					
[MMA] = $2.5 \text{ mol dm}^{-3}$ $[\text{K}_2\text{S}_2\text{O}_8] = 2 \times 10^{-2},$ $\text{mol dm}^{-3}$  [MPTC] = $2 \times 10^{-2},$ $\text{mol dm}^{-3}$  $[\text{H}^+] = 0.2$ $\text{mol dm}^{-3}$  $[\mu] = 0.05 \text{ mol dm}^{-3}$  Temp. = $50^\circ\text{C}$  Time = 50 min	Cyclohexanone (18.3)*	Chlorobenzene (5.7)*	Ethyl Acetate (3.91)*	Toluene (2.5)*	Benzene (2.4)*	Cyclohexane (1.13)*
	2.6	2.12	1.88	1.65	1.59	1.41

\*Dielectric constant

**Table 8**  
**Dependence of  $\bar{P}_n$  on MMA**

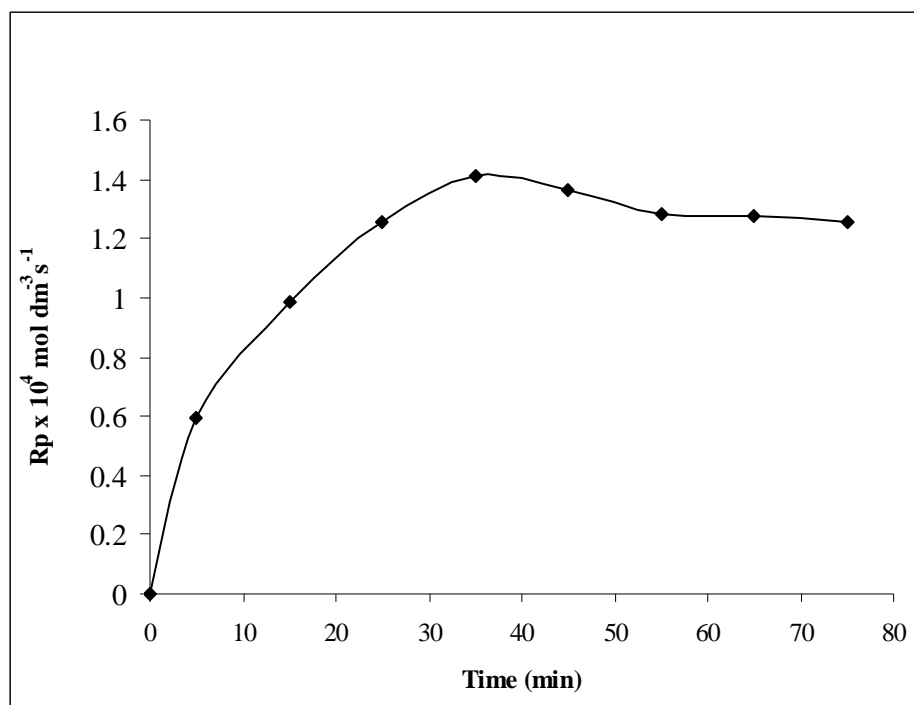
[MMA], mol dm <sup>-3</sup>	$\bar{P}_n \times 10^{-3}$	$1/\bar{P}_n \times 10^3$
1	4.82	0.21
1.5	3.27	0.31
2	2.5	0.40
2.5	1.94	0.52
3	1.72	0.58
3.5	1.54	0.7
4	1.35	0.80

**Table 9**  
**Dependence of  $\bar{P}_n$  on [K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>]**

[S <sub>2</sub> O <sub>8</sub> <sup>2-</sup> ] x 10 <sup>2</sup> , mol dm <sup>-3</sup>	[S <sub>2</sub> O <sub>8</sub> <sup>2-</sup> ] <sup>0.5</sup> x 10 <sup>2</sup> , [mol dm <sup>-3</sup> ] <sup>0.5</sup>	$\bar{P}_n \times 10^{-3}$	$1/\bar{P}_n \times 10^3$
1	10	4.55	0.22
2	14.14	3.13	0.32
4	20	2.44	0.41
5	22.36	2.08	0.48
6	24.49	1.85	0.54
8	28.28	1.61	0.62

**Table 10**  
**Dependence of  $\bar{P}_n$  on [MPTC]**

$[\text{MPTC}] \times 10^2, \text{ mol dm}^{-3}$	$[\text{MPTC}]^{0.5} \times 10^2, [\text{mol dm}^{-3}]^{0.5}$	$\bar{P}_n \times 10^{-3}$	$1/\bar{P}_n \times 10^3$
1	10	4.35	0.23
2	14.14	3.23	0.31
4	20	2.22	0.45
5	22.36	2.00	0.50
6	24.49	1.75	0.57
8	28.28	1.54	0.65



**Figure – 1**

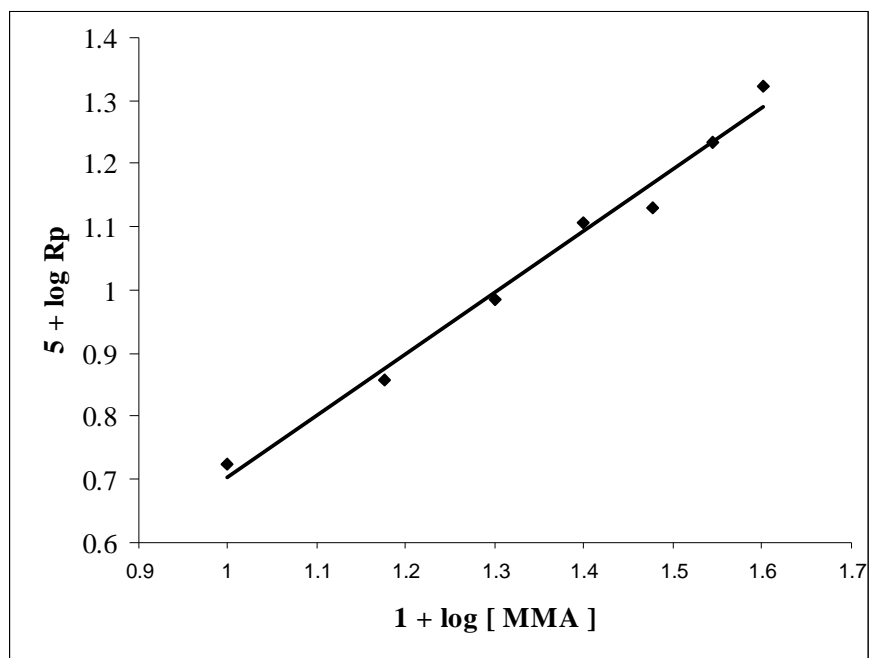


Figure 2

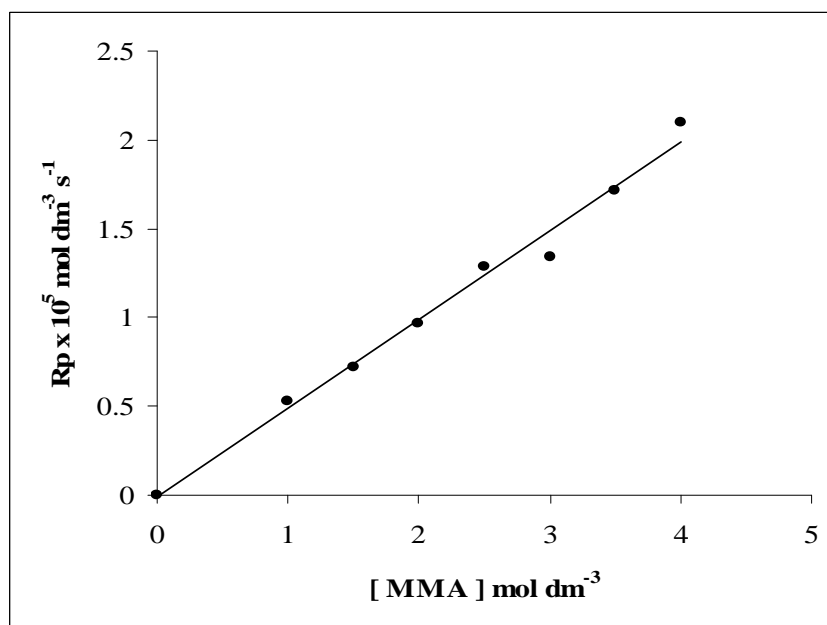


Figure 3

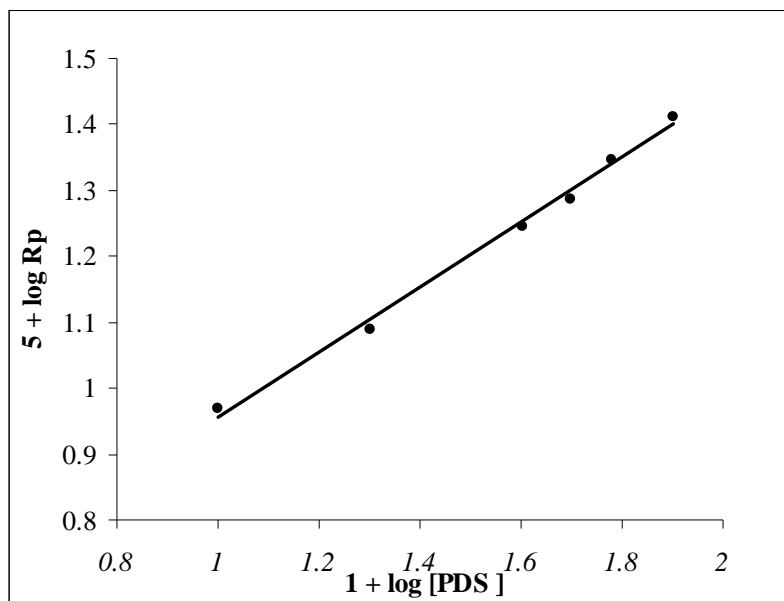


Figure 4

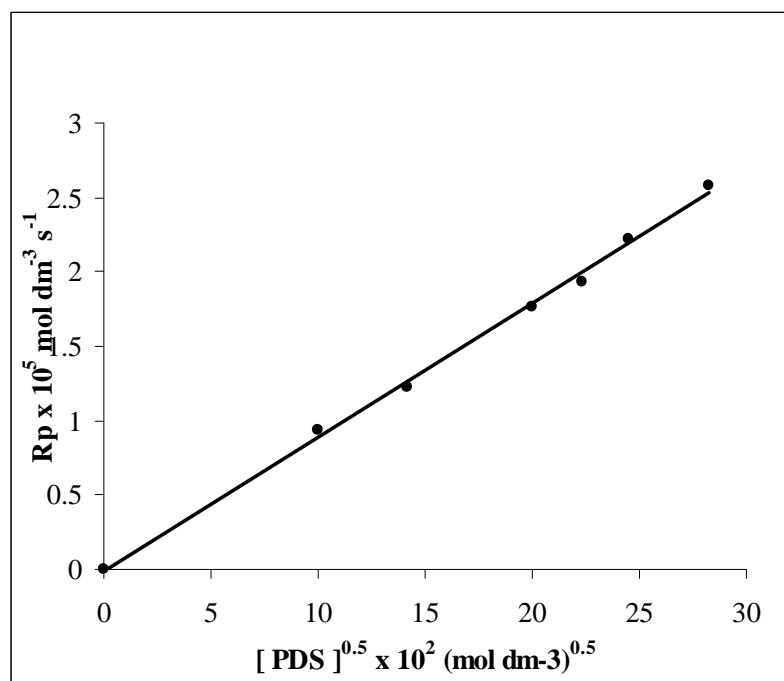


Figure 5

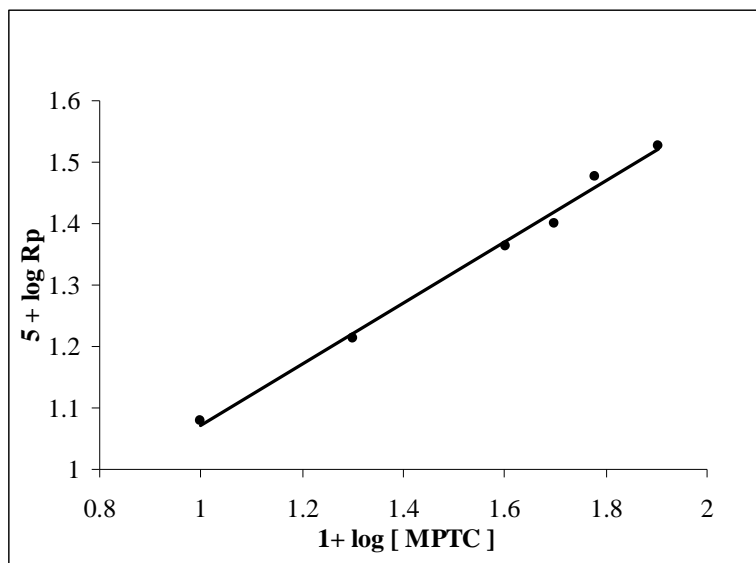


Figure 6

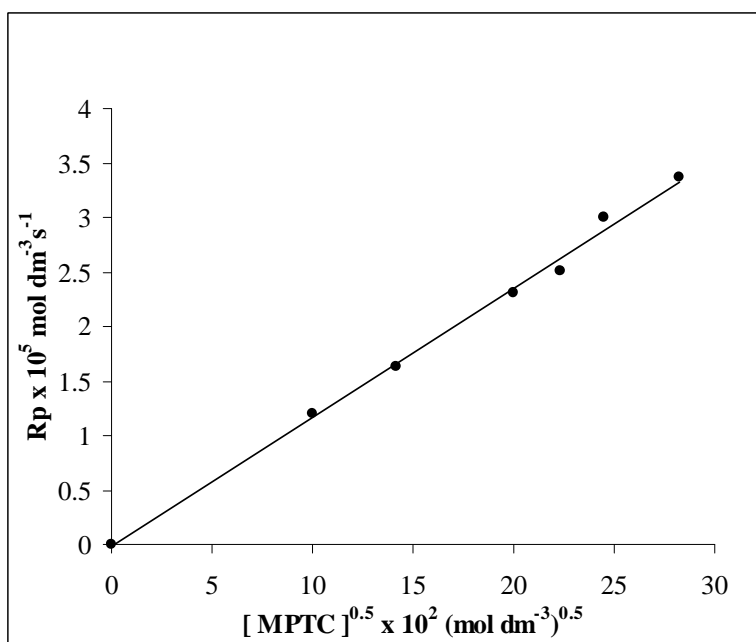


Figure 7



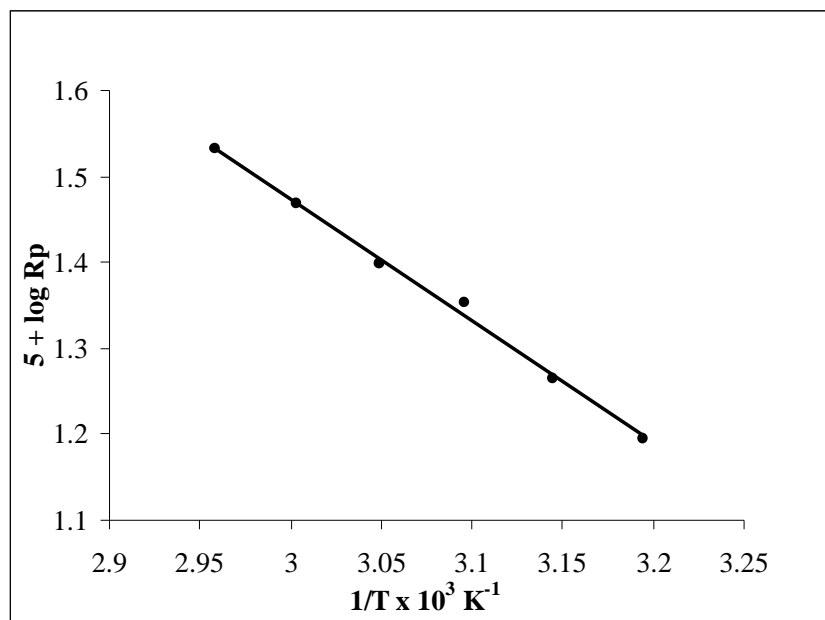


Figure 8

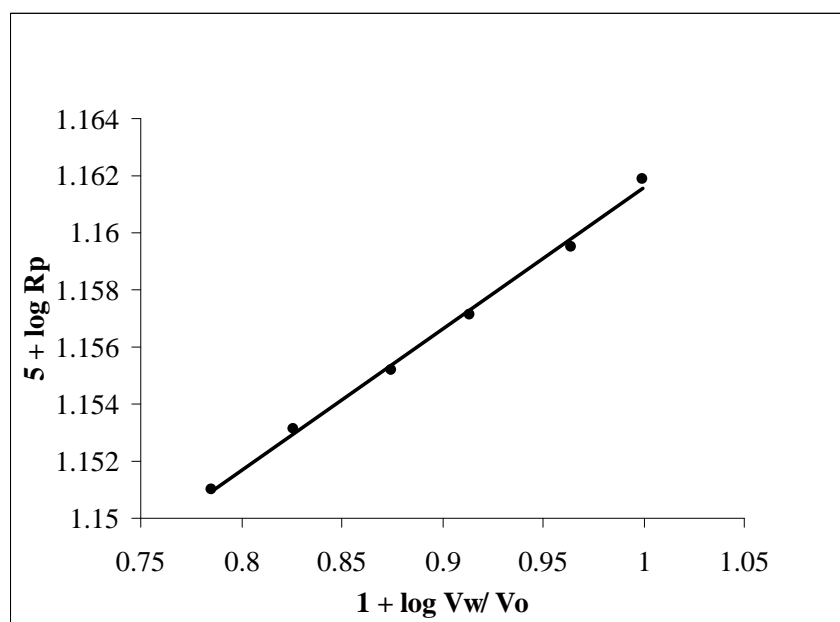


Figure 9

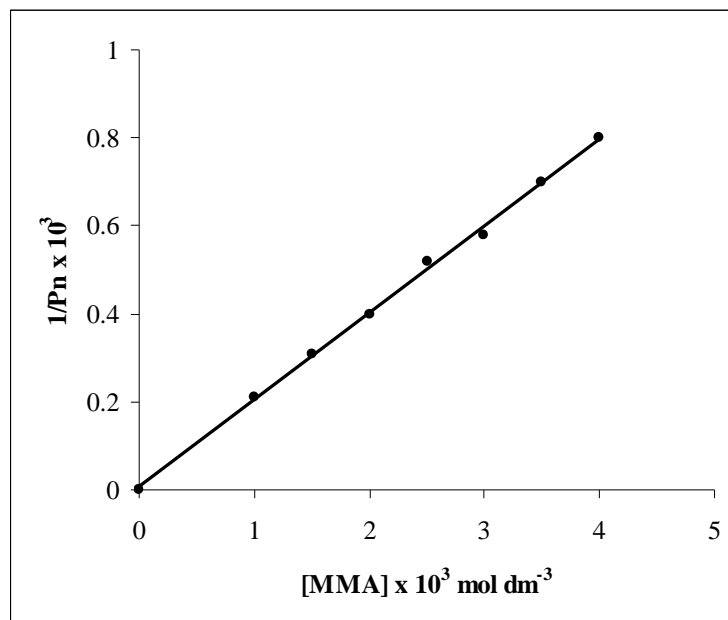


Figure 10

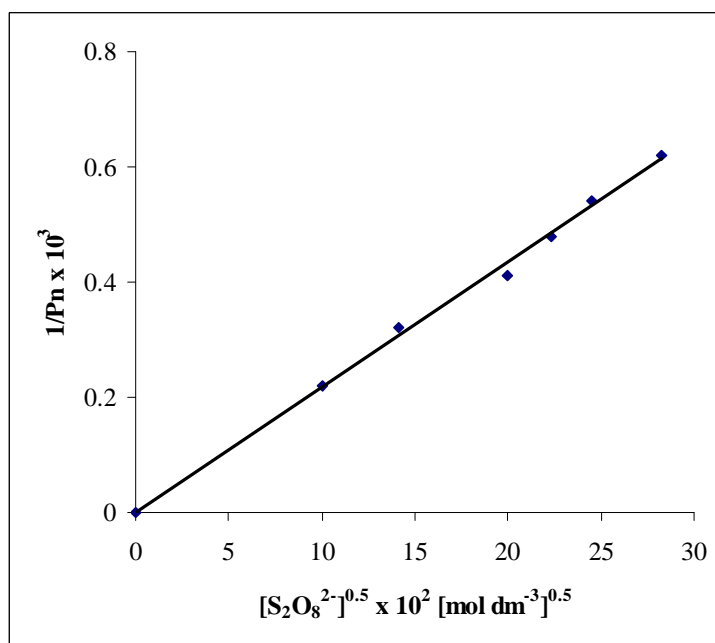


Figure 11

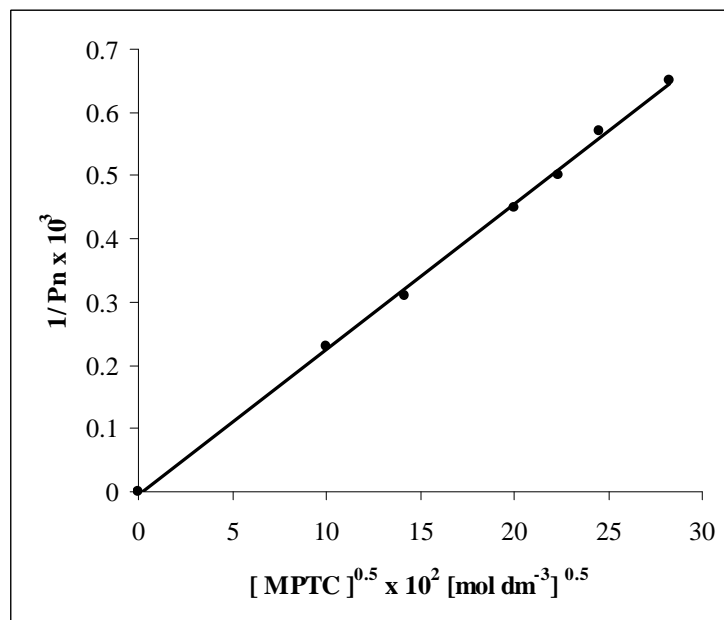
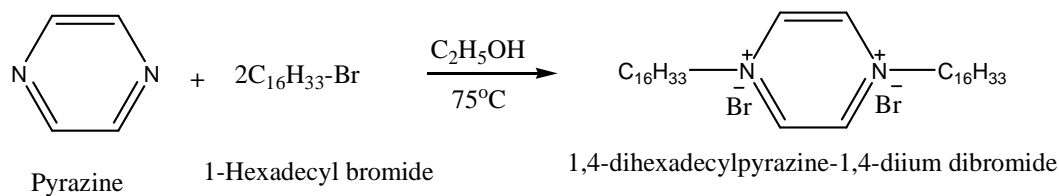


Figure 12



Scheme 1

## CONCLUSION

In this work, a new di-site phase-transfer catalyst has been synthesized, characterized and subjected to the study of kinetics and mechanism of the free radical polymerization of methyl methacrylate. The polymerisation reactions were carried out under inert atmosphere at constant temperature of 50°C in ethyl acetate / water biphasic medium using K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> as the water soluble initiator. The dependence of rate of polymerization (R<sub>p</sub>) on various experimental

conditions such as different concentrations of monomer, initiator, catalyst, and ionic strength, temperature and volume fraction of aqueous phase were discussed. From the Arrhenius plot, energy of activation (E<sub>a</sub>) and other thermodynamic parameters have been calculated. Based on the kinetic results obtained, a suitable mechanism has been proposed.

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